


AD-A281 419

## REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 1994		3. REPORT TYPE AND DATES COVERED Final 22 Apr 91-21 Apr 94	
4. TITLE AND SUBTITLE  Synthesis, Structure and Properties of Segmented Polymers Containing Mesogens				5. FUNDING NUMBERS  DAAL03-91-G-0127	
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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSORING / MONITORING AGENCY REPORT NUMBER  ARO 28314.10-CH	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.					
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.				12b. DISTRIBUTION CODE  DTIC SELECTED JUL 13 1994 S B D	
13. ABSTRACT (Maximum 200 words)  The purpose of the research carried out under Contract Number DAAL-03-91-G-0127 was to determine the phase behavior and to explore the conditions for thermodynamic stability in polyurethanes containing mesogens. The work involved both segmented polyurethanes with the mesogens residing in the hard segments, and model non-segmented polyurethanes containing mesogenic groups. In addition, molecular simulation techniques were brought to bear upon the problem of the structure of the mesogen containing polyurethanes and the phase diagram of segmented polyurethanes with hard segments containing rigid (diacetylene) moieties.					
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14. SUBJECT TERMS  Polyurethanes, Mesogens, Segmented Polyurethanes				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT  UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE  UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT  UNCLASSIFIED	20. LIMITATION OF ABSTRACT  UL		

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DTIC QUALITY INSPECTED 5

The research was a cooperative venture among three members of the Polymer Science and Engineering Department at the University of Massachusetts. R.J. Farris studied the thermodynamics of deformation and the processing of the polyurethanes to produce high degrees of orientation in both films and fibers. S.L. Hsu concentrated on molecular characterization using vibrational spectroscopy. He also was largely responsible for the molecular simulation efforts. W.J. MacKnight conducted the synthesis, characterization, mechanical and thermal properties, and morphology studies.

SYNTHESIS, STRUCTURE AND PROPERTIES  
OF SEGMENTED POLYMERS CONTAINING MESOGENS

FINAL REPORT

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JUNE 1994

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CONTRACT DAAL03-91-G-0127

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## A. Statement of the Problem

The purpose of the research carried out under Contract Number DAAL-03-91-G-0127 was to determine the phase behavior and to explore the conditions for thermodynamic stability in polyurethanes containing mesogens. The work involved both segmented polyurethanes with the mesogens residing in the hard segments, and model non-segmented polyurethanes containing mesogenic groups. In addition, molecular simulation techniques were brought to bear upon the problem of the structure of the mesogen containing polyurethanes and the phase diagram of segmented polyurethanes with hard segments containing rigid (diacetylene) moieties. The research was a cooperative venture among three members of the Polymer Science and Engineering Department at the University of Massachusetts. R.J. Farris studied the thermodynamics of deformation and the processing of the polyurethanes to produce high degrees of orientation in both films and fibers. S.L. Hsu concentrated on molecular characterization using vibrational spectroscopy. He also was largely responsible for the molecular simulation efforts. W.J. MacKnight conducted the synthesis, characterization, mechanical and thermal properties, and morphology studies.

## B. Summary of the Most Important Results

(1) Polyurethanes containing the mesogen 4,4'-bis(6 hydroxyhexoxy) biphenyl (BHHP) exhibit mesophases of the smectic type, as does the BHHP itself. The nature of the mesophases is primarily dictated by the packing requirements of the biphenyl ring in the BHHP and the hydrogen bonding present in the polyurethanes is of only secondary importance.

(2) Most BHHP containing polyurethanes do not possess a thermodynamically stable mesophase (i.e. they are of the monotropic type). The mesophase can be stabilized by structural modification of the diisocyanate. For example, polyurethanes based on the mixed diisocyanates 2,4 and 2,6 toluene diisocyanate (2,4 TDI and 2,6 TDI) exhibit stable smectic c mesophases over wide temperature ranges and do not possess stable crystal phases.

(3) By combining the molecular simulation method with Monte Carlo techniques, phase diagrams for various model segmented polyurethanes, especially those containing diacetylenic moieties in the hard segments, have been predicted. It was found that the rigidity of the hard segment plays an important role and that hydrogen bonding is not the driving force for phase separation. The results call into question some previously reported data on phase compositions based on glass transition temperatures of the soft segments.

(4) Segmented polyurethanes with hard segments composed of the BHHP mesogen and mixtures of 2,4 and 2,6 TDI exhibit an enantiotropic mesophase in the microphase separated hard domains. This mesophase is less highly ordered than commonly appears to be the case with structures containing BHHP. (It appears to be a nematic mesophase rather than a smectic mesophase). It can be oriented by elastic deformation and it forms a more ordered structure during the deformation. The

mechanical properties of these segmented polyurethanes are determined by their morphologies and can be manipulated by controlling the hard and soft segment concentration ratio.

C. List of Publications

Macromolecules 25, 925 (1992) (C.W. Meuse, X. Yang, D. Yang and S.L. Hsu), "Spectroscopic Analysis of Ordering and Phase-Separation Behavior of Model Polyurethanes in a Restricted Geometry"

Macromolecules 25, 2381 (1992) (S.K. Pollack, G. Smyth, F. Papadimitrakopoulos, P.J. Stenhouse, S.L. Hsu and W.J. MacKnight), "Development of Crystallinity in a Semiflexible Thermotropic Polyurethane. 2. Structure and Dynamics"

Macromolecules 25, 2391 (1992) (S.A. Nitzsche, S.L. Hsu, P. T. Hammond and M.F. Rubner), "A Spectroscopic Study of Domain Ordering in Diacetylene-Containing Model Polyurethanes"

Macromolecules 25, 2397 (1992) (S.A. Nitzsche, Y.K. Wang and S.L. Hsu), "Application of the Molecular Simulation Technique for Clarification of the  $\alpha$  -  $\beta$  Phase Transformation in Poly(butylene terephthalate)"

Macromolecules 25, 3667 (1992) (C.F. Fan, B.D. Olafson, M. Blanco and S.L. Hsu), "Application of Molecular Simulation to Derive Phase Diagrams of Binary Mixtures"

Macromolecules 25, 4672 (1992) (F. Papadimitrakopoulos, S.L. Hsu and W.J. MacKnight), "Investigation of a Monotropic Liquid Crystal Polyurethane Based on Biphenol, 2,6-Tolylene Diisocyanate, and a Six Methylene Containing Flexible Spacer. 1. Thermal and Structure Characterization"

Macromolecules 25, 4682 (1992) (F. Papadimitrakopoulos, E. Sawa and W.J. MacKnight), "Investigation of a Monotropic Liquid Crystal Polyurethane Based on Biphenol, 2,6-Tolylene Diisocyanate, and a Six Methylene Containing Flexible Spacer. 2. IR Spectroscopic Phase Characterization"

Makromol. Chem., Macromol. Symp. 69, 41 (1993) (W.J. MacKnight and F. Papadimitrakopoulos), "Phase Behavior and Structure in Mesogen Containing Polyurethanes"

Macromolecules 27, 2814 (1994) (W. Tang, R.J. Farris, W.J. MacKnight and C.D. Eisenbach) "Segmented Polyurethanes with Liquid Crystalline Hard Segments. 1. Synthesis and Phase Behavior"

D. List of All Participating Scientific Personnel and Degrees Awarded

<u>Personnel</u>	<u>Degree</u>
Professor Shaw Ling Hsu	-
Professor Richard J. Farris	-
Professor William J. MacKnight	-
Dr. M. Bellinger	-
Dr. Chon-Shin Jou	-
Dr. X. Li	-
Dr. J. Pionteck	-
Dr. Y-K. Wang	-
H. Akashi	-
K. Bakeev	Ph.D.
C-C. Chen	-
B. Chien	-
Elliot Douglas	Ph.D.
Chris Haak	M.A.
M. Lindway	Ph.D.
D. Macon	-
C. Meuse	Ph.D., Chemistry
J. Neill	Ph.D.
C-W. Ng	-
S. Nitzsche	-
J. Preuschen	-
Y. Ren	-
F. Papadimitrakopoulos	Ph.D.
J. Savage	Ph.D. Chemistry
W-M. Tang	-
S. Tandon	-
H-J. Tao	Ph.D.
J. Vrtis	-
W. Walczak	Ph.D.
S. Yoon	-

<b>Accession For</b>	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
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<b>Availability Codes</b>	
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